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## **Quantum mechanical studies of carbon structures**

Norman C. Bartelt, Donald K. Ward, Xiaowang Zhou, Michael E. Foster, Peter A. Schultz, Bryan M. Wong, and Kevin F. McCarty

Prepared by  
Sandia National Laboratories  
Albuquerque, New Mexico 87185 and Livermore, California 94550

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## **Quantum mechanical studies of carbon structures**

N.C. Bartelt<sup>1</sup>, D.K. Ward<sup>2</sup>, X.W. Zhou<sup>3</sup>, M.E. Foster<sup>4</sup>, P.A. Schultz<sup>5</sup>, B.M. Wong<sup>6,7</sup>, and Kevin F. McCarty<sup>6</sup>

<sup>1</sup>Materials Physics Department  
Sandia National Laboratories  
P.O. Box 969

Livermore, CA 94551-0969-MS9161

<sup>2</sup>Radiation and Nuclear Detection Materials and Analysis Department  
Sandia National Laboratories

<sup>3</sup>Mechanics of Materials Department  
Sandia National Laboratories

<sup>4</sup>Materials Chemistry Department  
Sandia National Laboratories

<sup>5</sup>Multiscale Science Department  
Sandia National Laboratories

<sup>6</sup>Previous member of Sandia National Laboratories

<sup>7</sup>Chemical and Environmental Engineering, Materials Science and Engineering  
University of California Riverside

### **Abstract**

Carbon nanostructures, such as nanotubes and graphene, are of considerable interest due to their unique mechanical and electrical properties. The materials exhibit extremely high strength and conductivity when defects created during synthesis are minimized. Atomistic modeling is one technique for high resolution studies of defect formation and mitigation. To enable simulations of the mechanical behavior and growth mechanisms of C nanostructures, a high-fidelity analytical bond-order potential for the C is needed. To generate inputs for developing such a potential, we performed quantum mechanical calculations of various C structures.



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## NOMENCLATURE

di	dimer
tri	trimer
ch	chain
tetra	tetragon
sq	square
dc	diamond-cubic
sc	simple-cubic
bcc	body-centered-cubic
fcc	face-centered-cubic
hcp	hexagonal-closely-packed
gra	graphite
grap	graphene
MD	molecular dynamics
DFT	density functional theory
PAW	projector-augmented-wave
VASP	Vienna Ab initio Simulation Package
vdW	van der Waals
GGA	generalized-gradient approximation
PBE	Perdew, Burke and Ernzerhof density functional

## 1. INTRODUCTION

Carbon nanostructures, such as nanotubes and graphene, are of considerable interest due to their mechanical and electrical properties. To develop defect free C nanostructures, predictive molecular dynamics (MD) simulations of C growth mechanisms are very valuable. Such simulations require a high-fidelity C interatomic potential [1]. To generate reference data for parameterizing the C potential, we performed quantum mechanical calculations to determine the cohesive energy and structural properties of various configurations of C. For convenience, we will use the following abbreviations to represent structures: di: dimer; tri: trimer; ch: chain; sq: square; tetra: tetragon; dc: diamond-cubic; sc: simple-cubic; bcc: body-centered-cubic; fcc: face-centered-cubic; hcp: hexagonal-closely-packed; gra: graphite; grap: graphene.



## 2. QUANTUM MECHANICAL METHODS

All density functional theory (DFT) calculations were performed within the spin-polarization formalism using the optB86b-vdW functional [2] and projector-augmented-wave (PAW) [3, 4] pseudopotentials. The optB86b-vdW functional was used because of its ability to capture dispersion interactions (van der Waals forces) which are essential for modeling the intramolecular interactions in C based systems (e.g. the interactions between graphene sheets in graphite); moreover, this functional has been shown to improve over transition generalized-gradient approximation (GGA) functionals (e.g. PBE) for a range of solids on the prediction of lattice constants, cohesive energies, and bulk moduli [2]. For all calculations a plane-wave cutoff energy of 500 eV was used and full geometry optimizations (ions and unit cell) were performed until all forces were smaller than 0.01 eV/Å. For bulk lattices, the Brillouin zone was sampled using a  $10 \times 10 \times 10$  gamma-centered Monkhorst-Pack grid [5]. For small clusters, the calculations are carried out in a  $25 \text{ Å}^3$  box using a gamma-point Brillouin zone. All calculations were performed within VASP 5.3.5 [6, 7, 8, 9].

### 3. RESULTS

The energies and atomic spacings of various clusters, consisting of four or less atoms for the elemental C are given in Table 1. The cohesive energies and atomic volumes of various elemental C lattice structures are given in Table 2. It should be noted that the experimental values for C structures [10, 11] are in good agreement.

**Table 1. Cohesive energies  $E_c$  (eV/atom) and atom spacing  $r$  (Å) of various C clusters. For chain  $r$  values, the first value is the exterior bond length and the second number is the internal bond length.**

Structure	C	
	$E_c$	$r$
tetra	-3.9410	1.5065
square	-4.6471	1.4664
trimer	-4.8444	1.3753
dimer	-3.4625	1.3127
chain	-5.2705	1.3175, 1.2958

**Table 2. Cohesive energies  $E_c$  (eV/atom) and lattice constants  $a$ ,  $c$  (Å) for selected lattices. Experimental values are given in parenthesis [10, 11]**

Structure	DFT	
	$E_c$	$a, c$
bcc	-3.8272	2.3745
dc	-8.0186 (-7.38)	3.5619 (3.56)
fcc	-3.6094	3.0884
gra	-8.0581 (-7.4)	2.465, 6.3949 (2.46, 6.69)
grap	-7.9919	2.4644
hcp	-4.1203	1.71965, 6.1473
sc	-5.2387	1.7517

### **3. SUMMARY**

This work presents a database of energies and geometric parameters for a range of structures for elemental C. The values are determined from DFT and were used for parameterizing interatomic potentials for MD simulations [1].



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